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Anisotropy in the electronic structure of V₂GeC investigated by soft x-ray emission spectroscopy and first-principles theory

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The anisotropy of the electronic structure of ternary nanolaminated V₂GeC is investigated by bulk-sensitive soft x-ray emission spectroscopy. The measured polarization-dependent emission spectra of V L₂,₃, C K, Ge M₁, and Ge M₂,₃ in V₂GeC are compared with those from monocarbide VC and pure Ge. The experimental emission spectra are interpreted with calculated spectra using ab initio density-functional theory including dipole transition matrix elements. Different types of covalent chemical bond regions are revealed: V 3d-C 2p bonding at −3.8 eV, Ge 4p-C 2p bonding at −6 eV, and Ge 4p-C 2s interaction mediated via the V 3d orbitals at −11 eV below the Fermi level. We find that the anisotropic effects are high for the 4p valence states and the shallow 3d core levels of Ge, while relatively small anisotropy is detected for the V 3d states. The macroscopic properties of the V₂GeC nanolaminates result from the chemical bonds with the anisotropic pattern as shown in this work.

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I. INTRODUCTION

In the last few years, a group of ternary nanolaminated carbides and nitrides denoted MXₙ₋₁AXₙ (MAX phases), where n=1, 2, and 3 refers to 211, 312, and 413 crystal structures, respectively, has attracted much attention.1 Here, M denotes an early transition metal; A is a p element, in groups IIIA and IVA; and X is either carbon and nitrogen.2 The MAX-phase compounds exhibit a unique combination of metallic and ceramic properties, such as low density, high strength and stiffness at high temperatures, resistance to oxidation and thermal shock, in addition to high electrical and thermal conductivities.3 The hexagonal crystal structures of the ternary MAX-phase compounds (space group P6₃/mmc) are closely related to the binary monocarbides and nitrides (MX). In spite of the structural similarities with the binaries, MAX phases exhibit very different chemical and physical properties. This is directly attributed to the anisotropic nanolaminated crystal structure with alternating strong M-X bonds and much weaker M-A bonds.3,4 The binary Mₙ₊₁Xₙ nanoscale blocks are interleaved with square-planar monolayers of pure A elements, where the X atoms (C or N) fill the octahedral sites between the M atoms. The A elements are located at the center of trigonal prisms that are larger than the octahedral X sites.5–8

Macroscopic properties such as electrical and thermal conductivity and elasticity of ternary carbides and nitrides are known to strongly depend on the valence-electron concentration of the M element. Information about the internal electronic structure and the anisotropic pattern of the chemical bonds is therefore invaluable but generally difficult to obtain experimentally. Previous experimental investigations of the electronic structure and chemical bonding of the 211 crystal structure mainly include Ti-based compounds such as Ti₃AlC(Ref. 9) and Ti₃AlN.10 For investigating the trend in the anisotropy of the chemical bond scheme, the nature of the electric and thermal conduction, and elastic properties, it is of great scientific interest to replace Ti with a heavier 3d element such as V. For this purpose, we have synthesized and investigated epitaxial V₂GeC and VC films grown on Al₂O₃(0001) single crystals. Figure 1 shows the crystal structure of V₂GeC with thermodynamically stable binary V-C-V blocks separated by softer V-Ge-V blocks with weaker bonds. Intercalation of Ge monolayers into the VC matrix implies that the strong V-C bonds are broken up and replaced by the weaker V-Ge bonds. Thus, in V₂GeC, every second layer of C atoms in VC has been replaced by a Ge monolayer, in effect resulting in understoichiometric VC. The VC blocks are then twinned with the Ge layers acting as mirror planes. The 211 crystal structure of V₂GeC contains anisotropic V atoms (octahedral coordination in plane and trigonal prismatic coordination out of plane) with chemical bonds both to C and Ge atoms, while stoichiometric VC monocarbide contains isotropic V atoms (octahedral coordination only) which only bond to C.

In the present paper, we investigate the anisotropy in the nanolaminated internal electronic structure of V₂GeC in comparison with those of monocarbide VC and pure Ge. Bulk-sensitive and element-specific soft x-ray emission (SXE) spectroscopy with selective excitation energies around the V 2p, C 1s, Ge 3s, and Ge 3p absorption thresholds is utilized. The involvement of both valence levels and different kinds of core levels makes it possible to study each of the constituent elements separately in the ternary compound. Changing the polarization of the electric field vector (E) of the incoming radiation effectively enables obtaining directional information about the chemical bonding, which cannot easily be obtained with other methods. We present an elec-
Electronic structure investigation of V$_2$GeC, which is particularly important for understanding and predicting the macroscopic properties. The SXE spectra are interpreted in terms of partial density of states (pDOS) weighted by the dipole transition matrix elements.

II. EXPERIMENT

A. Deposition of the V$_2$GeC and VC films

Figure 2 (top) shows θ-2θ x-ray diffractograms (XRD) of the deposited V$_2$GeC and VC$_x$ films. The V$_2$GeC(0001) (5000 Å thick) and VC$_x$(111) (x~0.875, 2000 Å thick) films were epitaxially grown on Al$_2$O$_3$(0001) substrates at 700 and 500 °C, respectively, by dc magnetron sputtering. Elemental targets of V, C, and Ge and a 3.0 mTorr Ar discharge were used.

Comparing the diffractograms of the V$_2$GeC (Fig. 2, top) and VC$_x$ (bottom) films, peaks of {000l} type from the V$_2$GeC MAX phase are observed together with VC$_x$(111) and substrate peaks. The VC$_x$ phase has a cubic NaCl (B1-type) crystal structure and is known not to exhibit any diffraction peaks at 2θ=18.4° and 57.4° as shown in the VC$_x$ diffractogram at the bottom of Fig. 2. However, at substoichiometric compositions and elevated temperatures, a disorder-order transformation occurs. The ordered structure consists of eight B1-type unit cells and has a total superstructure composition of V$_2$C$_7$ (i.e., VC$_{0.875}$).

In the V$_2$C$_7$ superstructure, the diffraction peaks at 2θ=18.4° and 57.4° are allowed, as observed in the top diffractogram in Fig. 2. The relative intensity of the V$_2$C$_7$ superstructure peaks compared to other VC$_x$ peaks increase with increasing deposition temperature. This suggests that the V$_2$GeC MAX-phase film contains a small mixture of disordered VC$_x$ and ordered V$_2$C$_7$ inclusions. In the following we will simply refer to the minor fraction of VC$_x$ monocarbide inclusions as VC$_x$. The formation of the VC$_x$ inclusions is due to the very narrow homogeneity range and the growth mechanism during the sputtering process. Minor fluctuations in the surface composition during the crystal growth lead to more favorable formation of VC$_x$ inclusions, segregation, and enrichment of Ge at the surface, causing renucleation. These self-regulated growth fluctuations have also been observed in other MAX-phase systems such as Ti-Al-C.

For the V$_2$GeC film, x-ray pole figures show that the VC$_x$ inclusions are coherent with the MAX phase showing an out-of-plane orientation VC$_x$(111)//V$_2$GeC(0001). The fact that the V$_2$GeC diffractogram (Fig. 2, top) shows mainly V$_2$GeC of {000l} type suggests a highly textured or epitaxial MAX-phase film. X-ray pole figures verified that the growth indeed was epitaxial with an in-plane orientation of V$_2$GeC(1010)//Al$_2$O$_3$[2130] and an out-of-plane orientation of V$_2$GeC(0001)//Al$_2$O$_3$(0001). The values of the a axis and c axis were determined to be 2.99 and 12.28 Å, respectively, by reciprocal space mapping. X-ray photoelectron spectroscopy (XPS) analyses of the V$_2$GeC and VC$_x$ films using a PHI Quantum instrument showed after 60 s of Ar sputtering a constant composition. Except for a thin surface oxidation of approximately 5 nm, no contamination species such as oxygen was detected in the bulk of the films by XPS depth profiling.

B. X-ray emission and absorption measurements

The soft x-ray absorption (SXA) and SXE measurements were performed at the undulator beamline I511–3 at MAX II (MAX-laboratory National Laboratory, Lund University, Sweden), comprising a 49-pole undulator and a modified...
The SXE spectra were calculated within the single-particle transition model by using the augmented plane wave plus local orbitals band-structure method.\textsuperscript{18} Exchange and correlation effects were described by means of the generalized gradient approximation as parameterized by Perdew et al.\textsuperscript{19} We previously successfully modeled SXE for MAX phases using similar methodology and obtained excellent agreement with experiment.\textsuperscript{8,10,26,27} giving credence to the present predictions for the $V_2$GeC system.

The total energy was first converged against the $k$-point integration ($21 \times 21 \times 4$), whereafter the theoretical emission spectra within the electric-dipole approximation were computed. We utilized a plane-wave cutoff corresponding to $R_{MT} \times K_{max} = 8.0$ and a muffin-tin radius of 1.90 a.u. for $V$, Ge, and C. The core-hole lifetimes employed in these calculations were 0.40, 0.12, 2.0, and 2.0 eV for the $2p$ and $1s$ and Ge $3s$ and $3p$ edges, respectively. Finally, we achieved a direct comparison of the calculated spectra with the measured data by including an instrumental broadening in the form of Gaussian functions (see Sec. II B). The final-state lifetime broadening was accounted for by a convolution with an energy-dependent Lorentzian function with a broadening increasing linearly with the distance from the Fermi level according to the function $a + b(E-E_F)$, where the constants $a$ and $b$ were set to 0.01 eV and 0.05 (dimensionless).\textsuperscript{22}

### B. Balanced crystal orbital overlap population

In order to study the chemical bonding of the $V_2$GeC compound, we calculated the balanced crystal orbital overlap population (BCOOP) functions by using the full-potential linear muffin-tin orbital method.\textsuperscript{23} In these calculations, the muffin-tin radii were kept as large as possible without overlapping each other ($V=2.2$ a.u., Ge=2.2 a.u, and C =1.6 a.u.). To ensure a well-converged basis set, a double basis with a total of four different $k^2$ values were used. For $V$, we included 4$s$, 4$p$, and 3$d$ as valence states. To reduce the core leakage at the sphere boundary, we also treated the 3$s$ and 3$p$ core states as semicore states. For Ge, 4$s$, 4$p$, and 4$d$ were taken as valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well-converged basis.\textsuperscript{24} For the sampling of the irreducible wedge of the Brillouin zone, we used a special-$k$-point method\textsuperscript{25} and the number of $k$ points were 1000 for $V_2$GeC and 1728 for VC in the self-consistent total energy calculation. In order to speed up the convergence, a Gaussian broadening of 20 mRy width was associated with each calculated eigenvalue.

### IV. RESULTS

#### A. V $L_{2,3}$ x-ray emission

Figure 3 (top, right curves) shows $V 2p_{3/2,1/2}$ SXA spectra of $V_2$GeC and VC measured to identify the photon energies of the absorption intensity peak maxima. The SXA measurements mainly probe the unoccupied $V 3d_{xy}$ and $3d_{x^2−y^2}$ in-plane orbitals. In the middle of Fig. 3, $V L_{2,3}$ SXE spectra of $V_2$GeC and VC are shown. The $E∥a, b$ excited SXE spectra predominantly probe the occupied $V 3d_{xy}$ and $3d_{x^2−y^2}$ in-plane orbitals. With $E∥c$ polarization, there is more influence from the out-of-plane $V 3d_{z^2}$ orbitals. In the $V L_{2,3}$ spectra of $V_2$GeC excited at 560.0 eV, four peaks are observed at $-2, -9, -11$, and $-19$ eV below $E_F$. For the nonresonant spectra (560 eV) of both $V_2$GeC and VC, an $O K$ emission peak at 525 eV on the photon energy scale at the top is observed. This peak appears for all excitation energies above the O $1s$ absorption edge at 543.1 eV and originates from a thin surface oxide layer on the samples. As the excitation energy is tuned resonantly to the $V 2p_{3/2}$ and $2p_{1/2}$ absorption maxima at 516.9 and 522.1 eV, the $V L_3$ and $V L_2$ spectral intensity resonates at the main peaks at $-11$ and $-2$ eV, respectively. In $V L_{2,3}$ spectra of pure $V$ (not shown), the peaks at $-11$ and $-19$ eV are absent and the main $L_3$ peak is located at $-9$ eV. The main peaks of the $V L_{2,3}$ SXE spectra of $V_2$GeC and VC are quite different in shape. The difference is the relative intensity of the $-11$ eV substructure, which is significantly higher in VC than in $V_2$GeC. This can be attributed to the pure octahedral coordination in VC in combination with the electronic structure of...
the V$_2$GeC spectra, the anisotropy is attributed to the difference in coordination between the V atoms in plane (octahedral coordination) and out of plane (trigonal prismatic coordination).

The V L$_{2,3}$ SXE spectra appear delocalized (wide bands) which makes electronic structure calculations particularly suitable for interpretation of nonresonant spectra. The calculated spectra (dotted curves at the bottom of Fig. 3) consist of V 3d and 4s pDOS obtained from full-potential ab initio density-functional theory projected by the 3d, 4s → 2p dipole transition matrix elements and broadening corresponding to the experiment. The core-hole lifetime broadening is set to 0.4 eV both for the 2p$_{3/2}$ and 2p$_{1/2}$ thresholds. To account for the L$_2$→L$_M$ Coster–Kronig decay which change the initial core-hole population from the statistical single-particle result (2:1), preceding the SXE process, the calculated spectra are fitted to the experimental L$_2$/L$_3$ ratio of 4.3:1. Furthermore, the 2p$_{3/2,1/2}$ spin-orbit splitting was set to the experimental SXE value of 8.2 eV. The 2p$_{3/2,1/2}$ core-level XPS spin-orbit splitting is 7.6 eV while the ab initio value is smaller (7.1 eV). The calculated ab initio values of the spin-orbit splittings in band-structure calculations are generally underestimated for the early transition metals (in this case 7.1 eV for V 2p) and overestimated for the late transition metals. The reason for this is not presently known, but must represent effects beyond effective one-electron theory, e.g., many-body effects. In Fig. 3, the fitted spin-orbit splitting was set to the experimental L$_{2,3}$ SXE value of 8.2 eV, while the 2p$_{3/2,1/2}$ core-level SXE spin-orbit splitting is 7.6 eV. The integrated areas of the experimental and calculated spectra were normalized to the calculated V 3d+4s charge occupations of V$_2$GeC (3d: 2.452e; 4s: 2.067e), and VC (3d: 2.389e; 4s: 2.070e). The area for the L$_2$ component was scaled down by the branching ratio and added to the L$_3$ component.

The final fitted spectra of V$_2$GeC and VC are in fairly good agreement with the experimental results, although the intensity distribution is somewhat different in the experiment. For VC, the L$_3$ double peak structure is in good agreement but a calculated peak at ~4 eV is not present in the experiment, which may partly be explained by the larger experimental 2p$_{1/2}$ lifetime broadening. For V$_2$GeC, the intensities of the −9 and −1 eV peaks are overestimated and the −11 eV peak underestimated in the calculation. Since the calculations do not include polarization effects, some of the differences in the intensities between experiment and theory may be attributed to the involvement of nonspherically symmetric V 2p core states and 3d valence states. However, part of the difference may also be due to the existence of the coherent VC$_x$ inclusions. The origin of the −11 eV peak is due to the L$_3$ component of a V 3d pDOS peak at −3.3 eV below E$_p$ which is shifted −8.2 eV by the 2p spin-orbit splitting. The much weaker 3d pDOS contribution at −3.3 eV stemming from the L$_2$ component overlaps with the stronger L$_3$ emission line at −2 eV. The origin of the −9 eV peak is related to the L$_3$ component of a series of flat bands of V 3d character resulting in high pDOS close to the E$_p$, shifted −8.2 eV by the 2p spin-orbit splitting. The −2 eV peak, which is most intense at 522.1 eV excitation energy, corresponds to the L$_3$ component of the V 3d pDOS, and the spectral shape is broader and less pronounced than the L$_3$.
The SXE spectra are excited with the polarization vector both parallel and perpendicular to the surface normal at 284.2 eV (resonant) and 310 eV (nonresonant). For each excitation energy, the spectra are normalized to the time and incoming photon flux from a gold mesh in the photon beam. The excitation energy of the absorption intensity peak maxima. The SXA measurements indicate the total resolution of 0.5 eV in the calculated spectra of V$_2$GeC and VC were normalized to the calculated C 2p charge occupations of V$_2$GeC (2p: 2.360 eV) and VC (2p: 2.317 eV). Calculated C K emission spectra including the C 2p pDOS projected by the 2p $\rightarrow$ 1s dipole transition matrix elements and broadening corresponding to the experiment are shown at the bottom of Fig. 4. The general agreement between the experimental and theoretical spectra is good with a few exceptions. The predicted −6 eV shoulder in the VC spectra does not exist experimentally, neither at nonresonant nor at resonant excitation energy. Moreover, the predicted peak structure at −0.5 eV in the calculated spectrum of VC is not visible experimentally.

C. Ge $M$ x-ray emission spectra

The top panel of Fig. 5 shows experimental Ge $M_1$ SXE spectra, following the 4p $\rightarrow$ 3s dipole transitions of V$_2$GeC and single-crystal Ge(001). The probability of the Ge $M_1$ transitions occurring is about 2 orders of magnitude lower than that for Ge $M_{2,3}$ emission, which makes the measurements demanding. For Ge in V$_2$GeC and pure Ge, the valence band is dominated by the Ge 4p$_z$ and 4p$_{xy}$ orbitals, oriented parallel and perpendicular to the surface normal $c$ (see Fig. 1). Starting with V$_2$GeC, the $M_1$ spectra (within 20 eV from the $E_F$) exhibit two main peaks observed at −6 and −11 eV. For comparison, the $M_1$ spectra of pure Ge shown below exhibit a peak at −2 eV with a shoulder at −6 eV. With $E||a$, $b$ polarization, mainly the occupied Ge 4p$_{xy}$ orbitals are probed. With $E||c$ polarization, there is more influence from the out-of-plane 4p$_z$ orbitals. The angular-dependent anisotropy of the Ge $M_1$ emission is large at −6 eV in V$_2$GeC, while it is absent in pure Ge. The intensity of the −6 eV peak is 3.7 times higher for $E||a$, $b$ polarization than for $E||c$ polarization. The absence of the −2 eV peak in V$_2$GeC may be caused by a combination of hybridization at lower energy, charge transfer, and final-state screening. The peak structures observed at −32 to −34 eV in the $M_1$ spectra correspond to 3$d$ $\rightarrow$ 3$s$ quadrupole transitions. These transi-
tions are angular dependent with opposite peak intensities in comparison to the 3d → 3p dipole transitions, which will be discussed in connection to the lower panel of Fig. 5. Due to the low transition probability, the quadrupole transitions exhibit a lower signal-to-background ratio than the dipole transitions. They appear at a somewhat lower energy than the corresponding dipole transitions in the lower panel, which can be attributed to final-state effects and screening. For comparison of the M1 peak intensities and energy positions, the integrated areas of the experimental and calculated spectra of V2GeC and VC were normalized to calculated Ge 4s, 4p, 3d, and 4d charge occupations in V2GeC (4p: 0.655e) and pure Ge (4p: 0.675e). The area for the M2 component was scaled down by the experimental branching ratio and added to the M1 component. The calculated Ge M1 spectrum of V2GeC was shifted by −3.47 eV, corresponding to the calculated screening effects by the energy difference between the 3d9 and 3d10 configurations.

The bottom panel of Fig. 5 shows experimental Ge M2,3 SXE spectra of V2GeC and Ge(001). The 4s valence band within 20 eV from the EF in the lower panel consists of a weak double structure with M1 and M2 emission structures observed around −11 and −5 eV, respectively. As observed, the 4s valence-band structure is significantly more intense in V2GeC than in pure Ge. Due to screening and charge transfer, there is a −1.1 eV low-energy chemical shift of the Ge 3p1/2 and 3p3/2 XPS binding energies in V2GeC (120.6 and 124.7 eV, respectively) in comparison to pure Ge (001) (121.7 and 125.8 eV, respectively). The −1.1 eV shift is significantly larger than the corresponding −0.3 eV shift observed for the Ge 3p1/2 and 3p3/2 XPS binding energies in Ti3GeC.20 The shallow 3d core level has XPS binding energies of 28.4 and 29.6 eV for V2GeC and Ge, respectively. The 3d level consists of two peaks from the Ge M4,5 → M1 and M4 → M2 (3d → 3p3/2,1/2) transitions with energies of −33.0 and −29.3 eV relative to the EF. The measured M4/M2 intensity ratios of Ge in V2GeC are 1.65:1 with in-plane excitation and 1.92:1 with out-of-plane excitation. For pure Ge, the ratios are 1.65:1 for the in-plane excitation and 1.62:1 for the out-of-plane excitation, which are all smaller than the statistical single-particle ratio of 2:1.

The calculated isotropic spectra are shown in the bottom panel of Fig. 5 by the full and dashed lines, both for the 4s valence band (full curves) and the 3d core levels (dashed curves). For comparison of the peak intensities and energy positions, the integrated areas of the experimental and calculated spectra of V2GeC and VC were normalized to the calculated Ge 4s, 3d, and 4d charge occupations in V2GeC (4s: 0.764e; 3d+4d: 9.867e) and pure Ge (4s: 0.747e; 3d+4d: 9.859e). For pure Ge, the calculated 4s DOS of the M3 and M2 valence bands are not only separated by the spin-orbit splitting of 3.6 eV, but are also split up into two sub-bands, separated by 3.5 eV (similar to the case of single-crystal bulk Si). The result is a triple structure in the valence band of Ge(001) where the upper and lower emission peaks are solely due to M3 and M2 emission bands, respectively, while the main middle peak is a superposition of both M3 and M2 contributions. On the contrary, the Ge 4s DOS in V2GeC consists of a single peak structure with more spectral weight toward the EF, resulting in a double structure in the calculated M2,3 emission. The measured Ge M2,3 spin-orbit splitting of 3.6 ± 0.1 eV (Ref. 26) is smaller than the calculated value of 4.3 eV and the calculated 3d core levels (dashed curves) are also closer to the EF by 3.9 eV.

D. Chemical bonding

Figure 6 shows the calculated BCOOPs (Ref. 27) of V2GeC and VC. The calculated orbital overlaps make it possible to compare the strength between covalent chemical bonds. A positive function below EF means covalent bonding states and a negative function above EF means antibonding states. The relative strength of the covalent bonding at a specific energy relative to the EF is determined by comparing the integrated areas under the curves. Increasing the energy
For both systems, the main $V_3$ peaks are significantly more complicated than for the binary VC. In Sec. IV A, the BCOOP calculations show that strong overlap has filled bonding orbitals up to the EF, means that a larger strength of covalent bonding is achieved. The V$_2$GeC SXE spectra of V$_2$GeC in comparison to VC. The −11 eV peak in the M$_1$ SXE spectra of V$_2$GeC appears at the same energy position as the −19 eV peak in the V 3$d$ spectra when the 8.2 eV V 2$p$ spin-orbit splitting is subtracted. However, the orbital overlap calculations show no sign of V 3$d$-Ge 4$p$ interactions at −11 eV. The −11 eV peak structure probably originates from the noncovalent anti-bonding V 3$d$-C 2$s$ interaction giving rise to charge transfer from the C 2$s$ orbitals to the Ge 4$p$ orbitals at the bottom of the valence band.

We find that the integrated intensity of the V 3$d$-Ge 4$p$ BCOOP curve at the −2.9 eV peak is 16% larger than the corresponding Ti-Al peak at −0.64 eV in Ti$_2$AlC. This shows that the V-Ge bonding in V$_2$GeC is stronger than the Ti-Al bonding in Ti$_2$AlC, as also indicated by the shorter bond length in Table I. Note that the V-C bond length in V$_2$GeC is shorter than in the monocarbide VC. This is an interesting finding which has been observed in other MAX phases and plays a key role for the physical properties of the material. However, due to the difference in atomic radii between V and Ti, there is no clear relationship between bond lengths and bond strengths in this case. Therefore it is more useful to compare V$_2$GeC with VC.

V. DISCUSSION

The intercalation of Ge monolayers into the VC matrix mainly changes the character and scheme of the chemical bond regions as mentioned above, but also close to the EF, where the conductivity occurs. The additional charge density introduced by hybridization with the Ge $sp$ bands leads to increased metallicity (decreased resistivity). The conductivity is largely governed by the V metal bonding and is roughly proportional to the total number of states at the EF (VC: 0.65 states/eV per atom; V$_2$GeC: 0.56 states/eV per atom; TiC: 0.12 states/eV per atom; and Ti$_2$AlC: 0.34 states/eV per atom). In reality, the V$_2$GeC film has significantly higher conductivity i.e., lower resistivity (0.21 $\mu\Omega$m) compared to Ti$_2$AlC [0.44 $\mu\Omega$m (Ref. 28)]. The resistivity of VC is even higher (0.93 $\mu\Omega$m) and for TiC an order of magnitude higher [2.00 $\mu\Omega$m (Ref. 29)]. From previous studies of ternary carbides, it is clear that those Ti atoms which are bonded to both C and the A element contribute more to the conductivity than the Ti atoms, which bond solely to C. Since V$_2$GeC contains only V atoms bonded to both C and Ge, one would expect that V$_2$GeC has higher conductivity.

<table>
<thead>
<tr>
<th>Bond type</th>
<th>$M_{T-C}$</th>
<th>$M_{H-C}$</th>
<th>$M_{H-A}$</th>
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<td>2.634</td>
<td>2.634</td>
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<tr>
<td>Ti$_2$AlC</td>
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<td>2.901</td>
<td>3.875</td>
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<tr>
<td>TiC</td>
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</table>

The calculated bond lengths (Å) for V$_2$GeC, Ti$_2$AlC, VC, and TiC. $M_{T}$ (octahedral coordination) is bonded only to C, while $M_{H}$ (octahedral in plane and trigonal prismatic coordination out of plane) is bonded to both C and the A element as illustrated in Fig. 1.
than ternary carbides with 312 and 413 crystal structures. In addition, there is a strong dependence of the valence-electron concentration for the $M$ element.

In Figs. 3–6, we identified three main types of covalent chemical bonds, the strong V 3d-C 2p bond, the V 3d-Ge 4p bond, and the V 3d-C 2s bond. The V 3d-C 2p and V 3d-C 2s hybridizations are deeper in energy from the $E_F$ than the V 3d-Ge 4p hybridization, indicating stronger bonding. Strengthening the $M$-$A$ bonding should increase the stiffness of the material. A change in the elastic properties is achieved by the additional valence charge occupancy in V, in combination with the larger electronegativity and smaller atomic radius compared to those of Ti. A V 3d-Ge 4p chemical bond strengthening is indeed observed in the electronic structure of nanolaminate V$_2$GeC with the combination with the larger electronegativity and smaller atomic radius compared to those of Ti. A V 3d-Ge 4p chemical bond strengthening is indeed observed in the electronic structure of V$_2$GeC in comparison to the Ti 3d-Al 3p bonding in Ti$_2$AlC. This is consistent with the calculated Young’s modulus ($E$ modulus) of V$_2$GeC (334 GPa), which is higher than for Ti$_2$AlC (305 GPa). However, the measured $E$ modulus is lower in V$_2$GeC (189 GPa) than in Ti$_2$AlC [260 GPa (Ref. 31)]. The difference between the experimental and calculated $E$ moduli can be due to the coherent VC$_x$ inclusions in the V$_2$GeC film. The measured $E$ moduli of both V$_2$GeC and Ti$_2$AlC are both significantly lower than for VC [255 GPa (Ref. 31)] and TiC$_{0.8}$ [388 GPa (Ref. 32)]. Recently, it has been theoretically predicted that there is a linear relationship between the bulk moduli ($B$) of the ternary MAX phases and the corresponding binary compounds as the valence band of the constituent $M$ element is being filled.$^{34,35}$ Experimentally, for the $E$ modulus of single-crystal thin-film materials, the corresponding linear relationship is more complicated to assess as measurements are made in a certain direction of the material. Moreover, for the binary transition-metal carbides, it is theoretically known that the bond strength, bond energy, and enthalpy decreases as the 3d band of the constituent transition metal is being filled.$^{36,37}$

VI. CONCLUSIONS

In summary, we have investigated the anisotropy of the electronic structure of nanolaminate V$_2$GeC with the combination of polarization-dependent soft x-ray emission spectroscopy and electronic structure calculations. The measured emission spectra of V L$_{2,3}$, C K, Ge M$_{1,3}$, and Ge M$_{2,3}$ of V$_2$GeC were compared to monocarbide VC and pure Ge. Ge M$_{1}$ x-ray emission spectra of V$_2$GeC and pure Ge were presented. Different types of covalent chemical bond regions were revealed; V 3d-C 2p bonding at −3.8 eV, Ge 4p-C 2p bonding at −6 eV and Ge 4p-C 2s interaction mediated via the V 3d orbitals at −11 eV below the Fermi level. We found that the anisotropic effects were most pronounced for the Ge 4p valence states and the shallow Ge 3d core levels, while relatively small anisotropy was detected for the V 3d states. In comparison to single-crystal Ge, the $M_1$ x-ray emission spectra of V$_2$GeC exhibit more intensity and charge transfer to the 4$p_{z}$ in-plane valence-band orbitals than to the 4$p_{z}$ out-of-plane orbitals. The anisotropic pattern of the chemical bond regions as revealed for V$_2$GeC determines the electrical and thermal conductivity and the elastic properties of the material. As shown, measuring the polarization dependence of the electronic structure can be utilized as an advanced tool to probe the internal orbital hybridization with different symmetries and rigid bond directions in nanostructured materials.

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26 The 3.6 eV splitting in the measured emission spectra is consistent with the difference between the $3p_{3/2,1/2}$ and $3d_{5/2,3/2}$ spin-orbit splittings observed in XPS, i.e., 4.1–0.5 eV.
32 For TiC$_x$, $x=0.97$ exists in single phase. However, the eutectic point is $x=0.74$ and higher stoichiometry often results in an amorphous phase separation, more impurities, and stress, leading to higher modulus and hardness (Ref. 33).